Digital μ-fluidics
The flow of confined bubbles and drops
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Every drop/bubble is a test tube

Distribute

Optical valve
Baroud et al., Lab Chip (2007)

Split-up

Synchronize

Sort

Merge
Prakash et al., Science (2007)

Feedback
Prakash et al., Science (2007)

www.raindancetechnologies.com
Formation, mixing, merging, selection, …

Rapid variations with minimal sample use

Zheng *JACS* 125 (2003), 11170
High Throughput Nucleation Statistics
Single cell studies

Brouzes, *PNAS* 106 (2009), 14195
Lab-on-a-chip Chemistry

1. Reaction front
   - A reacts with B
   - Examples:
     - Direct fluorination
     - Phase transfer catalysis

2. Catalyst Y
   - A reacts with B in the presence of a catalyst Y
   - Examples:
     - Hydrogenation
     - Oxidation

3. Reaction occurs in A (or B) and B (or A) is a passive 'segmentation tool'

Kreutzer et al., Chem Eng Sci 60 (2005) 5895
Gunther et al., Lab Chip 6 (2006) 1487

Ismagilov, 2006
Motivation – Plug Flow & Rapid Mixing

Material Synthesis

\[ \tau = 14 \text{ min} \quad \textit{Khan, 2005} \]

Res. Time Distribution = Particle Size Distribution

High-Throughput Analytical Chemistry

Karger 2005

Kreutzer & Guenther, 2005
Residence Time distribution = Particle Size Distribution

Colloidal Silica. Khan *Langmuir* 2005

Segregation - Dispersion

Catalysis: film thickness key parameter

Excellent transport to wall

\[ \frac{d_{\text{film}}}{d_{\text{channel}}} = O(Ca^{2/3}) \approx 10^{-2} \]

100-fold better mass-xfer

Full CFD simulation

Michiel T. Kreutzer\textsuperscript{a,\,*}, Freek Kapteijn\textsuperscript{a}, Jacob A. Moulijn\textsuperscript{a}, Johan J. Heiszwolf\textsuperscript{b}

Chemical Engineering Science 60 (2005) 5895–5916
Segmented flow Synthesis

Kinetic tool, ideal for hazardous chemistry

\[ \text{Azide hydrogenation to form amines} \]

Temperature low enough to maintain stereospecificity
Monitoring conversion is easy

(a)

(b) flow

inlet

Conversion [%]

0 10 20 30 40 50 60 70 80 90 100

run 1 run 2

GC Camera GC Camera
Fast kinetics

Complete kinetics can be measured in a day

\[
0^{th} \text{ order in CE} \\
r \sim kC_{H_2}
\]

\[
1^{st} \text{ order in CE} \\
r \sim kKC_{H_2}C_{CE}
\]

\[
r = \frac{kKC_{H_2}C_{CE}}{1+KC_{CE}}
\]

\[E_a = -34 \text{ kJ/mol} \quad \left( R^2 = 0.99 \right) \]

\[E_a = -32 \text{ kJ/mol (Boudart et al. 1978)} \]
Our basic questions for today

• Simplest case: bubble/droplet in a tube
  – What is the flow resistance? Film thickness?
  – Look at the basic problem of forced wetting (plate, capillary, all the same)
  – Do the full matched-asymptotics that leads to the “BLL 2/3 law”

• More complex cases: inertia, marangoni effects?
  – Basic features of the solutions

• Channel Shape?
The Bretherton-Landau-Levich problem

Layer on flat plate  coating on a wire  coating in a tube

Characteristics:

- Film deposited, thickness depends on speed (so called “2/3-law”, thickness scales with $Ca^{2/3}$)
- Both on wetting and non-wetting surfaces (the transition to forced wetting is NOT today’s topic)
- Matching of film to “outer” solution
Basic setup of the problem - Matching

\[ \frac{\partial p}{\partial x} = \mu \frac{\partial^2 u}{\partial y^2} \]

Moving reference frame: bubble stands still: \[ u(0) = -U, \quad \frac{\partial u}{\partial y}(h) = 0 \]

Navier Stokes:

Continuity

with \[ q = \int_0^h u \, dy \]
Lubrication thin-film equation

Navier Stokes: \[ u = -U + \frac{\partial p}{\partial x} \left[ \frac{y^2}{2\mu} - \frac{yh}{\mu} \right] \]

Laplace pressure \[ \frac{\partial p}{\partial x} \approx \frac{\partial}{\partial x} \left[ \gamma \frac{\partial^2 h}{\partial x^2} \right] \]

Continuity \[ \frac{\partial h}{\partial t} + U \frac{\partial h}{\partial x} - \frac{\gamma}{3\mu} \frac{\partial}{\partial x} \left( h^3 \frac{\partial^3 h}{\partial x^3} \right) = 0 \]

q = \int_0^h u \, dy = Uh - \frac{\gamma}{3\mu} h^3 \frac{\partial^3 h}{\partial x^3}
Scaling of the transition region: first relation

\[
\frac{\partial h}{\partial t} + U \frac{\partial h}{\partial x} - \frac{\gamma}{3\mu} \frac{\partial}{\partial x} \left( h^3 \frac{\partial^3 h}{\partial x^3} \right) = 0
\]

Bubble stands still, so must be zero, we balance the 2\textsuperscript{nd} and 3\textsuperscript{rd} terms:

\[
\frac{\partial h}{\partial x} \sim \frac{\gamma}{3\mu U} \frac{\partial}{\partial x} \left( h^3 \frac{\partial^3 h}{\partial x^3} \right)
\]

\[
x \sim \lambda \quad h \sim \delta \quad \frac{\delta}{\lambda} \sim \frac{\lambda}{3\mu U} \frac{1}{\lambda^3} \left( \frac{\delta^3}{\lambda^3} \right)
\]

or

\[
Ca^{1/3} \sim \frac{\delta}{\lambda}
\]
Matching to outer solution: second scaling relation

First scaling rule

\[ Ca^{1/3} \sim \frac{\delta}{\lambda} \]

Scaling of the problem

\[ \delta \sim r Ca^{2/3} \]
\[ \lambda \sim r Ca^{1/3} \]

Second scaling rule

\[ \frac{\delta}{\lambda^2} \sim \frac{1}{r} \]

Matching curvature

flat film region | transition region | spherical cap region

\[ \kappa \sim \frac{\partial^2 h}{\partial x^2} \sim \frac{\delta}{\lambda^2} \]

\[ \kappa = \frac{1}{r} \]
The Bretherton-Landau-Levich problem

- **Clean interface case:**
  - 2/3 law experimentally predicted by Morey (1940)
  - Theoretical derivation of 2/3 law for flat plate by Landau-Levich (1942)
  - Theoretical derivation of 2/3 law for capillaries by Bretherton (1961)

- **Surfactant case**
  - Theoretical derivation by Bretherton (1961)
  - Coating of flat surfaces by Groenveld (1970)

- **Additional forces (on top of viscous-capillary)**
  - Gravity & Partial wetting fluids by Snoeijer (2008)
Master equation

Again, using the film evolution equation

$$\frac{\partial h}{\partial t} + \frac{\partial}{\partial x} \left( Uh - \frac{\gamma}{3\mu} h^3 \frac{\partial^3 h}{\partial x^3} \right) = 0$$

Steady state, so drop the transient term

$$Uh - \frac{\gamma}{3\mu} h^3 \frac{\partial^3 h}{\partial x^3} = c \quad \Rightarrow \quad \frac{\partial^3 h}{\partial x^3} = \frac{3\mu U}{\gamma} \frac{h - c}{h^3}$$

In the flat region, \( \frac{\partial^3 h}{\partial x^3} = 0 \)

which gives \( c \):

$$0 = \frac{\delta - c}{\delta^3}, \quad c = \delta$$

\eta = \frac{h}{\delta}

\xi = (3Ca)^{1/3} \frac{x}{\delta}

\frac{\partial^3 \eta}{\partial \xi^3} = \frac{\eta - 1}{\eta^3}
Forced Wetting Film Equation

\[ \frac{\partial^3 \eta}{\partial \xi^3} = \frac{\eta - 1}{\eta^3} \]

“exponential range”

\[ \eta \approx 1 \]

\[ \frac{\partial^3 \eta}{\partial \xi^3} \approx \eta - 1 \]

which has an analytical solution

\[ \eta = 1 + \alpha e^\xi + \beta e^{-\xi} \cos \left( \frac{3^{1/2}}{2} \xi \right) + \gamma e^{-\xi} \sin \left( \frac{3^{1/2}}{2} \xi \right) \]

“parabolic range”

\[ \eta \gg 1 \]

\[ \frac{\partial^3 \eta}{\partial \xi^3} \approx 0 \]

which has an analytical solution

\[ \eta = \frac{P}{2} \xi^2 + Q \xi + R \]
Four different regions with their scaling

\[
\frac{\partial^3 \eta}{\partial \xi^3} = \frac{\eta - 1}{\eta^3}
\]

\[
\frac{\partial^n \eta}{\partial \xi^n} = 0
\]

\[
\frac{\partial^3 \eta}{\partial \xi^3} \approx \eta - 1
\]

\[
\frac{\partial \eta}{\partial \xi} \ll (3Ca)^{-1/3}, \quad \frac{\partial^3 \eta}{\partial \xi^3} \approx 0
\]

\[
\frac{\partial^2 \eta}{\partial \xi^2} = \frac{\delta}{r(3Ca)^{2/3}}
\]
Set up match of "exp" and "parabolic"

Exponential: \( \frac{\partial^3 \eta}{\partial \xi^3} = \eta - 1 \)
\[ \eta(\xi) = 1 + \alpha e^\xi \]

Parabolic: \( \frac{\partial^3 \eta}{\partial \xi^3} \approx 0 \)
\[ \eta(\xi) = \frac{P}{2} \xi^2 + Q \xi + R \]
Use exponential for initial conditions:

\[ \eta(\xi) = 1 + ae^{-\xi} \]
\[ \eta(0) = 1 + a \]
\[ \eta'(0) = a \]
\[ \eta''(0) = a \]

And integrate full equation with that

\[ \frac{\partial^3 \eta}{\partial \xi^3} = \frac{\eta - 1}{\eta^3} \]

Move numerical solution to left and right, such that \( Q = 0 \)

Fitting:

\[ P = 0.643, \quad R = 2.79 \]

Note: MTK gets \( a = 0.001, \quad P = 0.643, \quad Q=0, \quad R = 2.90 \) with Mathematica’s NDSolve
2/3 law for film thickness

\[ \frac{\partial^3 \eta}{\partial \xi^3} = \frac{\eta - 1}{\eta^3} \]

\[ \frac{\partial^2 h}{\partial x^2} = \frac{1}{r} \]

is the same as

\[ \frac{\partial^2 \eta}{\partial \xi^2} = \frac{\delta}{r(3Ca)^{2/3}} \]

Parabola matches to the sphere:

\[ 0.643 = \frac{\delta}{r(3Ca)^{2/3}} \]

\[ \frac{\delta}{r} = 0.643(3Ca)^{2/3} \]
Perturbation of Laplace pressure

The parabola \( h = \left( \frac{x^2}{2} + 1.79(3Ca)^{2/3} \right) r \) matches to a sphere of curvature \( \left[ \frac{2}{r}(1 + 1.79(3Ca)^{2/3}) \right] \)

\[
\eta = 0.643\xi^2 + 2.79 \\
\frac{\eta}{r/\delta} \sim 1 \\
\frac{\partial^2 \eta}{\partial \xi^2} = \frac{\delta}{r(3Ca)^{2/3}} \\
\frac{\partial^n \eta}{\partial \xi^n} = 0
\]
Rear of the bubble

\[ \eta(\xi) = \frac{0.643}{2} \xi^2 - 0.8 \]

Numerical solution

\[ \eta = 1 + \alpha e^{-\xi} \cos \left[ \frac{3^{1/2}}{2} \xi \right] + \beta e^{-\xi} \sin \left[ \frac{3^{1/2}}{2} \xi \right] \]
Pressure drop over the bubble:

\[ \Delta p = [1 + 1.79(3Ca)^{2/3}] \frac{2y}{r} \]

\[ \Delta p = [1 - 0.46(3Ca)^{2/3}] \frac{2y}{r} \]

\[ \Delta p = 4.52(3Ca)^{2/3} \frac{y}{r} \]
Experiments

Bretherton, *J Fluid Mech* 10 (1961), 166
Why the maximum?

First matching rule
\[ Ca^{1/3} \sim \frac{\delta}{\lambda} \]

Second matching rule
\[ \frac{\delta}{\lambda^2} \sim \frac{1}{r - \delta} \] Thick film decreases radius of curvature!

Scaling of the problem
\[ \delta \sim r \frac{Ca^{2/3}}{1 + Ca^{2/3}} \]
\[ \lambda \sim r \frac{Ca^{2/3}}{[1 + Ca^{2/3}]^{1/2}} \]

The not-so-simple cases

Marangoni, Inertia, non-round, thick films, …
Marangoni Effects

Moving reference frame: bubble stands still:

\[ u(0) = -U, \quad \partial u / \partial y(h) = 0 \]

\[
\frac{\partial h}{\partial t} + U \frac{\partial h}{\partial x} - \frac{\gamma}{3 \mu} \frac{\partial}{\partial x} \left( h^3 \frac{\partial^3 h}{\partial x^3} \right) = 0
\]

\[ \delta = 0.643 \, r \left( 3 \text{Ca} \right)^{2/3} \]

\[ \delta = 0.643 \, r \left( 12 \text{Ca} \right)^{2/3} \]
Inertia changes bubble shape

$Ca = 0.04$

$Re = 1, 10, 100, 200$

Kreutzer et al, *AIChE* 51 (2005) 2428
Inertia increases film thickness

\[ \delta \sim r \frac{Ca^{2/3}}{1 + Ca^{2/3} - We} \]

\[ We = \frac{\rho U^2 (r - \delta)}{\gamma} \]


Square Channels

Modeling Shapes and Dynamics of Confined Bubbles

Vladimir S. Ajaev\textsuperscript{1} and G.M. Homsy\textsuperscript{2}

Rise of Liquids and Bubbles in Angular Capillary Tubes

José Bico and David Quéré\textsuperscript{1}


Hydrostatics

Without flow, there cannot be a gradient of (Laplace) pressure

\[ \nabla p = 0 \]

For a channel of width \( W \) and height \( H \), we have at the nose

\[ \Delta p = \gamma \left[ \frac{2}{H} + \frac{2}{W} \right]^{-1} \]

In the gutter, no curvature in the axial direction, so

\[ \Delta p = \gamma \left[ \frac{1}{\infty} + \frac{1}{\alpha} \right]^{-1} \]

\[ \alpha = \left[ \frac{2}{W} + \frac{2}{H} \right]^{-1} \]


Bretherton’s problem - MT Kreutzer
**Film Deposition**

![Diagram of fluid film deposition with annotations](Image)

- **Deposition region (1)**
  - $Ca^{1/3}$
  - $x \sim Ca^{-1}$ First stage of film rearrangement (3)

- **Tangential convection region (2)**
  - $O(1)$

- **Quasi-steady constriction (4)**
  - $Ca^{2/3}$
  - $x \gg Ca^{-1}$ Second stage (5)

- **Termination region (6)**
  - $h_1 Ca^{-1/3}$

The non-uniformity starts at the nose

\[ \delta = \frac{0.643}{\alpha} (3Ca \cos\phi)^{2/3} \]

What have we learned

- Scaling in flow of long bubbles / droplets in cylindrical tubes (basically the same as Landau Levich)

- Marangoni effects increase film thickness and pressure drop by a factor $4^{2/3}$

- There is a maximum film thickness at high Ca (this does not happen with a flat plate LL scaling)

- Inertia increases film thickness, numerical solution needed

- Square channels have highly non-uniform films
Further Reading

• Recent reviews


  Kreutzer et al., *Chem Eng Sci* 60 (2005) 5895


• Microfluidics: a couple of key papers
